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TERMS

DOE	U.S. Department of Energy
IC	ion chromatography
ICP	inductively coupled plasma
MCL	maximum contaminant level
MSDS	Material Safety Data Sheet
PCL	Process Chemistry Laboratory
PNL	Pacific Northwest Laboratory
QAPP	Quality Assurance Program Plan
TIC	total inorganic carbon
TOC	total organic carbon
WHC	Westinghouse Hanford Company

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WHC-SD-EN-TC-003, Rev. 0

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1.0 INTRODUCTION

These test procedures describe laboratory studies proposed to investigate $ex\ situ$ methods to remove chromate [chromium(VI) or Cr(VI)], nitrate (NO $_3$) and uranium [present as uranium(VI) or U(VI) species] from contaminated Hanford Site groundwaters. The technologies to be investigated, chemical precipitation or coprecipitation to remove chromate and uranium and anion exchange to remove chromate, uranium and nitrate, are identified in the 100-HR-3 Groundwater Treatability Test Plan (DOE-RL 1992a). Precipitation is not expected to remove nitrate from solution.

Precipitation-based removal of Cr(VI) (as well as associated metals such as zinc, nickel, cadmium, and copper) from plating bath wastes has been tested and implemented (Beller 1989). The process utilizes sodium sulfide (Na₂S) and ferrous sulfate (FeSO₄) to first reduce Cr(VI) to Cr(III) and then to (co)precipitate the reduced Cr(VI) with the resulting ferric hydroxide (Fe(OH)₃)/ferric sulfide (Fe_xS_y). The successful results of the implementation of this approach corroborate Westinghouse Hanford Company (WHC) laboratory studies in which Na₂S and FeSO₄ were used separately in the reduction and precipitation from solution of Cr(VI) (Thornton 1991). The method proposed by Beller (1989) will be tested for removal of Cr(VI) from Hanford Site groundwater. The possible reduction/precipitation and retention of U(VI) by this technique also may occur and will be tested. Removal of uranium from Hanford Site groundwaters and wastewaters by Fe(OH)₃ coprecipitation has been tested with promising results (Hodgson 1988).

Carrier precipitation of U(VI) by calcium hydrogen phosphate (brushite, CaHPO₄) has been implemented in treating uranium fuel fabrication plant waste solutions (Muller 1984). Thus, simple addition of disodium hydrogen phosphate (Na₂HPO₄) to precipitate brushite from the contained calcium ion naturally present in the Hanford Site groundwater will be tested for its efficacy in removing U(VI). Experiments may show, however, that additional calcium ion, introduced as calcium chloride (CaCl₂) solution to the groundwater, is required to provide sufficient precipitate to carry uranium. The incidental removal of Cr(VI) from solution by coprecipitation with brushite also will be checked.

The precipitation method(s) for Cr(VI) and uranium removal from the groundwater may be used in conjunction with a biodenitrification method for nitrate removal. Thus, an important subsequent objective shall be the successful integration of the proposed precipitation and biodenitrification steps.

Strong-base anion exchange has been used in separate approaches to remove Cr(VI) from corrosion inhibition solutions used in water-cooled heat exchange equipment and to remove nitrate from nitrate-polluted waters (Kirk-Othmer 1981a). Strong-base anion exchange also has been used successfully in uranium milling operations (Benedict 1981) as well as to remove U(VI) from contaminated Hanford Site groundwaters (Delegard 1986).

In the proposed tests, three strong-base anion exchange resins will be tested for their efficiency and capacity in removing the three contaminants (chromate, uranium and nitrate) from Hanford Site groundwater. Based on these tests, one, or possibly two, of the resins will be evaluated further for

breakthrough capacity and regeneration characteristics. The three resins were selected for these applications on the recommendations of the resin manufacturers, Rohm and Haas and Dow Chemical Company.

2.0 SCOPE AND OBJECTIVES

These test procedures identify all tests to be performed and the associated testing parameters, schedules, and data collection requirements. Also identified are the organizations responsible for the several tasks involved in this work and the locations the laboratory work will be performed. Included are the experimental designs and general procedures to be used in preparing the solutions and assembling the test apparatus. The objectives of these studies are summarized in Table 2-1 (DOE-RL 1992a).

Table 2-1. Test Objectives.

Reduct	ion/	'preci	ipita	tion
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Determine physical conditions and removal chemistry, and associated sludge generation quantities; determine reaction rates; determine effects of feed variability and presence of other contaminants; determine sludge characteristics, stabilization, and filtration qualities; determine if biodenitrification hinders precipitation or reduction reactions; determine co-removal of uranium.

Ion exchange

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Determine pretreatment requirements; determine optimum resin(s); determine falloff in loading after multiple cycles; determine resin regeneration requirements, and waste volumes and compositions.

3.0 REQUIREMENTS

The safety, quality assurance, reporting, equipments requirements and schedule for this task are elucidated below.

3.1 SAFETY REQUIREMENTS

Laboratory personnel will comply with the WHC Chemical Hygiene Program (WHC 1992) and other internal WHC industrial safety requirements. Special safety requirements identified in this test plan are associated with the use of solutions, solids and labware containing chromate and uranium. Handling of these materials will be conducted in fume hoods to eliminate inhalation hazards. The operator will wear rubber gloves as protection against absorption pathways through the skin.

Material Safety Data Sheets (MSDS) shall be utilized as a primary reference during the handling of the chemical materials used in the tests. The MSDS numbers for the chemical materials identified in the testing activities are listed in Table 3-1.

Table 3-1. MSDS Numbers for Materials.

<u>Chemicals</u>	Na ₂ CrO ₄	1486
	UO ₂ (NO ₃) ₂ • 6H ₂ O	2783
	NaNO ₃	1506
	FeSO ₄	2871
	Na ₂ S	1512
	Na ₂ HPO ₄	1886
	NaC1	1485
	NaHCO ₃	1480
	CaCl ₂	1087
	AgNO ₃	1472
Resins	IRA-402 [®] , Rohm and Haas	13688
	IRA-410°, Rohm and Haas	13538
	Dowex 21K°, Dow	10847

3.2 QUALITY ASSURANCE/QUALITY CONTROL AND DATA RECORDING REQUIREMENTS

The activities undertaken in this test procedure shall be performed in accordance with the quality assurance program plan (QAPP) for the Processing and Analytical Laboratories (WHC 1993). The QAPP is written to ensure compliance with the U.S. Department of Energy (DOE), Richland Field Office (RL) requirements for environmental restoration work (DOE-RL 1992b).

All data collected during the course of these testing activities shall be recorded on approved data sheets or in controlled laboratory notebooks issued through WHC Document Control. Data sheets shall be affixed into the laboratory notebooks. These records shall be reviewed and approved by supervisory personnel within the performing organizations in a timely manner and shall be organized and stored under controlled conditions maintained by the performing organizations. These records shall include identification of all key measuring devices and associated calibration records. Chain-of-custody records for samples and analytical records associated with samples also shall be maintained and stored in a controlled manner. Data and sample control activities shall be performed in accordance with QA requirements of the performing organizations and in a manner appropriate for an Impact Level 3Q developmental effort (i.e., in a manner consistent with standard laboratory practices with QA review). These records shall be available for review by representatives of the WHC Environmental Engineering Group.

Analyses of the chromium-, uranium-, and nitrate-containing solutions utilized in this work shall be obtained through WHC Analytical Laboratories to verify the concentrations of chromium, uranium, and nitrate being used and to check the stability of the solutions. A sample of the Hanford groundwater utilized in these experiments shall also be analyzed for cations (by inductively coupled plasma spectrometry (ICP)), anions (by ion chromatography (IC), total organic carbon (TOC), total inorganic carbon ((TIC), which is carbonate, ${\rm CO_3}^{2-}$), uranium, Cr(VI), and pH.

The reference numbers for the procedures used for chemical analyses are presented in Table 3-2. As these analyses may be performed at either 222-S or PUREX laboratories, method numbers for both laboratories are given where appropriate.

Table 3-2. Chemical Analyses.

Analyte(s)	Method #	Title	Minimum Detection Limit	Performance level*
Cations (ICP)	LA-505-151	ICP Emission Spectrometer Method for Trace Element Analysis of water and waste.	50 ppb	100 ppb Cr(VI)
chromium LA-505-241 Trace		ICP Emission Spectrometer Method for Trace Element Analysis of water and waste.	50 ppb	100 ppb Cr(VI)
Chromium(VI)	LA-265-101	Spectrophotometric determination of Cr(VI)	25 ppb	80 ppb Cr(VI)
Anion (IC) LA-533-105 LA-533-201		Anion analysis on Dionex Model 4000i	10,600 ppb	45,000 ppb nitrate
Nitrate	LA-533-105 LA-533-201	Anion analysis on Dionex Model 4000i	10,000 ppb	45,000 ppb nitrate
Uranium	LA-925-106	Determination of uranium by laser fluorimetry	1 ppb U	15 pCi/L gross alpha = 22 ppb uranium**
Total organic carbon	LA-344-105	Determination of carbon in solutions by combustion and coulometry	N/A	N/A
Total inorganic carbon	LA-622-102	Determination of carbonate/carbon or TIC in solutions by coulometry	N/A	N/A
Total alpha and total beta	LA-508-101	Alpha and beta in liquid sample		15 pCi/L gross alpha 40 pCi/L gross beta
pH	LA-212-102	Determination of pH direct measurement	N/A	N/A

^{*}Values from DOE 1992a.

^{**}Based on natural uranium.

N/A = Not Applicable

The precision and accuracy for all analyses will be 25% RPD and 75 to 125% recovery, respectively. Representativeness is addressed by using solutions which have concentrations that are similar to either regulatory performance levels or contamination levels found in 100 Area groundwaters. Comparability of the data generated will be discussed, where appropriate, in the final report.

3.3 REPORTING REQUIREMENTS

Original or high quality copies of all records generated during the testing activities shall be assembled as a project data file by the performing organization, the WHC Process Chemistry Laboratory (PCL). These data packages shall be transmitted to the WHC Environmental Engineering Group and shall be accompanied by letter reports describing the work performed. The results and conclusions obtained from the activities described in this test procedure shall be compiled and documented in a project report coauthored by representatives of the WHC Environmental Engineering Group and PCL. This report shall be completed and delivered to WHC management by 2 September 1993.

3.4 SCHEDULE

The schedule for these tasks has been defined in the treatability test plan (DOE-RL 1992a). The points in the schedule pertaining to the laboratory activities defined in this test procedure are summarized in Appendix A. Further activities related to this test procedure are outlined below.

<u>Task Name</u>	Start Date	<u>Duration, mo</u>
HA-3 Lab Test Report	1-Jun-93	5.5
Data Evaluation `	1-Jun-93	3
Submit report for review	2-Sep-93	0
WHC Review	5-Nov-93	1
RL/HQ Review	9-Dec-93	1.5
Issue Document	28-Jan-94	0

3.5 EQUIPMENT

Ordinary laboratory equipment will be used, which includes, but is not limited to centrifuges, stirrers, ion exchange columns, pumps, centrifuge tubes and pipetters.

4.0 PROCEDURE OVERVIEW

4.1 TREATMENT PARAMETER SELECTIONS

The goal of the tests described in this test procedure is to determine the efficacy of precipitation-based techniques in the removal of Cr(IV) and uranium and the efficacy of anion exchange in the removal of Cr(IV), uranium, and nitrate from Hanford Site groundwater. Steps involved in these activities include:

Precipitation Tests

- Collect uncontaminated Hanford Site groundwater, analyze for the analytes listed in Table 3-2 (except gross alpha and gross beta)
- 2. Spike chromate, U(VI) and nitrate into the uncontaminated groundwater in varying concentrations according to the statistical plan (Section 4.2)
- 3. Aliquot spiked groundwater and introduce precipitation agents, noting temperature.
- Mix treated groundwater samples thoroughly
- Collect, filter and analyze groundwater samples for Cr(VI), total chromium and uranium, analyze filter cake for volume and percent water.
- 6. Integrate and interpret results and select most effective precipitation agent
- 7. Treat fully spiked groundwater with selected precipitation agent and collect, filter and analyze groundwater samples, for Cr(VI), total chromium and uranium as a function of time, analyze filter cake for volume and percent water.
- Integrate and interpret results

Anion Exchange Tests

- Collect uncontaminated Hanford Site groundwater, analyze for the analytes listed in Table 3-2 (except for gross alpha and gross beta)
- 2. Spike Cr(IV), U(VI), and nitrate into the uncontaminated groundwater in varying concentrations according to the statistical plan
- 3. Condition resins to chloride form using NaCl solution
- 4. Aaliquot spiked groundwater and introduce conditioned resins
- 5. Agitate groundwater/resin samples thoroughly for 30 min
- Centrifuge groundwater/resin mixture, collect supernatant solution and analyze groundwater samples for Cr(VI), total chromium, uranium and nitrate
- Integrate and interpret results and select most effective resin
- 8. Perform breakthrough test on selected resin by pumping fully spiked groundwater through a resin column and collecting, filtering and analyzing effluent groundwater samples as a function of throughput volume

- 9. Perform load/elute cycling tests of selected resin to monitor resin stability
- 10. Integrate and interpret results.

4.2 CONFIRMATORY TESTING

Following the precipitation and anion exchange tests described above, confirmatory tests will be run using contaminated groundwaters obtained from wells 199-D5-15 (high chromium and low nitrate and radionuclides), 199-H4-4 (high nitrate and radionuclides but low chromium) and 199-H4-12 (low nitrate, chromium, and radionuclide contamination). These waters have been specified for testing (DOE-RL 1992a) and will be examined using selected precipitating agents, anion exchange resins, and treatment conditions delineated in the following sections.

The confirmatory testing will also include: (2) the use of groundwater after the beiodenitrification tests; (2) gross alpha and gross beta analyses; (3) pH before and after treatment regimes; and (4) gravity settling test (for flocculation basin parameters).

4.3 RESPONSIBILITIES

The WHC Environmental Engineering Group shall be responsible for project management activities and for step 1 in both sets of tests. The WHC Environmental Engineering Group shall also be jointly responsible, with the WHC PCL, in the integration and interpretation of results (steps 6 and 8 in the precipitation tests and steps 7 and 10 in the anion exchange tests). Personnel in the WHC Process Chemistry Laboratory shall perform the experimentation and shall submit the samples to the WHC Analytical Laboratories for analysis.

Personnel safety must be considered in handling the moderately hazardous materials involved in these tests. Protective rubber gloves shall be worn whenever working with Cr(IV)- or uranium-bearing materials or equipment. Any experimentation involving Cr(IV) or uranium must be conducted in a hood. All laboratory tests will be conducted at the 222-S laboratory. Analytical work will be conducted at 222-S/202-A (PUREX) laboratories.

4.4 PREPARATION OF SPIKED HANFORD SITE GROUNDWATER

Artificially contaminated Hanford Site groundwater shall be prepared by spiking uncontaminated Hanford Site groundwater with solutions containing Na_2CrO_4 , $UO_2(NO_3)_2$ and $NaNO_3$. The concentrations of spike contaminant in the test groundwaters are given in Table 4-1.

The spiked groundwaters will be used in both the precipitation and anion exchange tests. For both sets of tests, two-level, full-factorial experimental designs will be performed in which Cr(VI), U(VI) and NO_3 concentrations are the test factors run at high and low values. Thus, 2 x 2 x 2 = 8 different solution compositions will be prepared and used.

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Calutian Number	()	
Solution Number	Cr(VI)	U(VI)	NO ₂
1	2,000	800	200,000
2	2,000	800	2,000
3	2,000	40	200,000
4	2,000	40	2,000
5	50	800	200,000
6	50	800	2,000
7	50	40	200,000
8	50	40	2,000

Table 4-1. Concentrations of Spike Contaminants in the Test Solutions.

The lowest concentrations of Cr(IV) and uranium in these spiked groundwater solutions are values near the maximum contaminant level (MCL) for those species. The lowest value for nitrate was chosen to reflect a trace value for nitrate. The MCL for nitrate in drinking water is 45,000 ppb. This concentration is equivalent to about 0.73 mmol/L and is comparable with the concentrations of the anionic species naturally occurring in the Hanford Site groundwater; bicarbonate (HCO_3^- , 2 mmol/L), chloride (Cl⁻, 0.1 mmol/L) and sulfate (SO_4^{2-} , 0.1 mmol/L). Therefore, nitrate at the 45,000 ppb MCL level cannot be considered a chemically trace constituent in the groundwater whereas chromate and uranium at their respective MCL levels can.

To assess accurately the effects of nitrate on chromate and uranium treatment tests as well as not overwhelm the groundwater chemistry, the lower level of nitrate was selected to be, at 2,000 ppb, substantially lower than the MCL. The selected upper concentration, 200,000 ppb, is representative of many contaminated Hanford Site groundwaters.

It is noted that incidental nitrate will be admitted by using $\rm UO_2(NO_3)_2$ as the uranium spike. The quantity of $\rm NaNO_3$ added to the test solutions will be adjusted appropriately to compensate for the concentrations of nitrate introduced in this way.

4.5 PRECIPITATION TESTS

The precipitation tests will be undertaken using two candidate precipitating agents; a combined ferrous sulfate and sodium sulfide treatment and a disodium hydrogen phosphate treatment. The initial tests will be conducted in duplicate (two for each solution/precipitation agent combination) on the test solutions described in Table 4-1 and in centrifuge vials at about 10 to 20 mL solution volume per vial. Following introduction of the precipitating agent, a 30-min contact time is suggested during which glass-covered stirbar agitation will be used. After the 30-min contact, the suspensions will be centrifuged in the centrifuge vials and the volume and percent water of settled solids noted. A sample of the supernatant solution will be drawn via syringe

and filtration accomplished using syringe filters. These filters are made of cellulose or cellulose acetate and have nominal 0.45 μm pore size. Tests to determine filter adsorption of contaminants will be performed to demonstrate that the precipitating agents and not the filter are responsible for the reduction of the contamination.

The filtrates will be analyzed spectrophotometrically for Cr(VI) concentration using the diphenylcarbazide reagent. The concentrations of total chromium will be determined by ICP spectrometry and uranium concentration determined by laser fluorimetry while nitrate concentrations will be determined by IC. These determinations will be performed by Analytical Laboratory personnel.

Precipitation kinetics tests will be conducted in a similar experimental manner. In the kinetics test, solution number 1 (Table 4-1) will be treated with the selected precipitating agent(s) and stirbar agitation commenced. Aliquots will be drawn and filtered periodically at contact times as low as 1 min and as long as 24 hr. Duplicate runs will be conducted for each precipitating agent. Chemical analyses shall be conducted as described for the initial tests. Reduction of chromate by the ferrous sulfate and sodium sulfide treatment is expected to be rapid. The immediate spectrophotometric analysis for Cr(VI) therefore is imperative.

Duplicate precipitation kinetic tests will also be performed with the selected precipitation agent(s) on contaminated groundwater pretreated by a biodenitrification procedure. The tests will be identical to those conducted on solution number 1.

4.5.1 Ferrous Sulfate - Sodium Sulfide

The ferrous sulfate and sodium sulfide treatment is an evolution of a standard method used earlier for treating chromate-contaminated waters. The standard approach employs sulfuric acid (H_2SO_4) acidification and ferrous sulfate reduction followed by lime $(Ca(OH)_2)$ neutralization and precipitation. This approach is reviewed by Wikoff (1988).

Based on the experience of Beller (1989), and the related work reported by Wikoff (1988), the stepwise introduction of Na_2S solution at about 12 mg S^2 /L followed by $FeSO_4$ at about 10 mg Fe^{2^+}/L will be performed for Hanford Site groundwaters. This choice of reagent concentration follows Wikoff (1988) studies of streams, which most closely resemble the Hanford Site groundwaters. According to these studies, the ferrous and sulfide ions act both as reductants of $CrO_4^{2^-}$ and as coprecipitants, with Fe^{3^+} , of the resulting Cr^{3^+} ion. The reversible reaction

$$Fe^{2+} + Fe^{3+} + e^{-}$$
 (1)

also is thought to act as an electron shuttle (catalyst) between the chromate being reduced and the sulfide being oxidized.

The studies of Beller (1989) and Wikoff (1988) were undertaken with an eye towards application to an existing facility which relied on removal of the metal precipitates by gravity settling. Thus, addition of an anionic floccu-

lent was studied, and ultimately was implemented, as a means to coagulate the extremely fine and slowly settling sulfide and hydroxide precipitates. For the wastewater compositions studied by Wikoff (1988) closest to the compositions of the Hanford groundwaters, Betz 1120 (trademark of Betz Industrial, Trevose, Pennsylvania) was found to be the most effective, of the 20 or so flocculating agents tested, in coagulating the product floc.

Crossflow membrane filtration, however, has been successfully demonstrated in the removal of ferric hydroxide precipitants, without surfactants or flocculating agents, from Hanford Site groundwater and low-level wastewater streams (Hodgson 1988). In the design of an ex situ groundwater treatment process, an active solids-removal step such as crossflow filtration is required to achieve a high assurance of contaminant removal under operating conditions. For this reason, surfactant addition will not be investigated in the experimental program outlined here unless tests show adequate filtration performance is not achievable with the simple sodium sulfide-ferrous sulfate treatment. In that case, further investigations may be conducted to select a suitable flocculating agent.

4.5.2 Disodium Hydrogen Phosphate

The disodium hydrogen phosphate treatment has been utilized in the removal of uranium from process waste solutions from a fuel element fabrication plant in Germany (Muller 1984). The uranium concentrations evaluated in that study ranged from zero to 0.18 g U/L (for ammonium uranyl carbonate filtrate). The goal of the German treatment tests was to reduce the uranium activity to <370 Bq/L (equivalent to 10^4 pCi/L or 0.028 g/L). Treated AUC filtrates were reduced to as low as 900 µg U/L.

The goal of the present tests is to reduce the uranium concentration to less than 15 pCi/L (approximately 22 μg U/L). Laboratory studies of uranium removal from Hanford groundwater using brushite coprecipitation showed concentrations as low as 100 μg U/L could be obtained while phosphate treatment of dilute acidic uranium-bearing wastewaters contacting Hanford sediment yielded uranium solution concentrations <1 μg U/L (Appendix B and C).

Scouting tests will be conducted in which test solution number 1 described in Table 4-1 will be treated with a volume of Na_2HPO_4 solution equivalent in molar quantity to the calcium available in the groundwater aliquot. Supplemental addition of $CaCl_2$ solution, with equivalent additional Na_2HPO_4 solution, may be necessary to achieve satisfactory uranium and chromium decontamination. Therefore, scouting tests using solution number 1 will be conducted to determine what level of supplemental $CaCl_2$ and Na_2HPO_4 addition, if any, is required. Following the scouting tests, and if the test results are judged to be promising, the statistically designed initial tests and the kinetics tests will be conducted.

4.6 ANION EXCHANGE TESTS

Strong-base anion exchange removal of the targeted groundwater contaminants (nitrate, Cr(IV), and uranium) has been demonstrated, though not simultaneously. The technical literature regarding removal of uranium from carbonate solutions used in the dissolution of uranium values from in-place

ores (in situ leaching, Bibler (1989)), excavated ores (ex situ leaching, Benedict (1981) and Kirk-Othmer (1981b)), as well as in the remediation of groundwaters ((Delegard (1986) and Lee (1983)) is particularly prominent. The high affinity of the uranium species present in the Hanford groundwaters; the carbonato complexes, $\mathrm{UO_2(CO_3)_2}^{2^-}$ and $\mathrm{UO_2(CO_3)_3}^{4^-}$; for strong-base anion exchange resins is the key to the potential success of this approach.

Less well documented is the use of strong-base anion exchange in the removal of chromate and nitrate from contaminated waters. Treatment of municipal-supply contaminated well-water via anion exchange has been implemented to reduce nitrate concentrations to less than 23 mg NO_3 /L (Sheinker 1977). The goal in the present treatment tests is 45 mg NO_3 /L. The removal of Cr(IV) from corrosion inhibitor solutions used to condition water-cooled heat exchanger equipment has been implemented. Again, strong-base anion exchange has been the method of choice Kirk-Othmer (1981a).

4.6.1 Experimental Approach

Based on conversations with technical representatives of the resin manufacturers Rohm and Haas and Dow Chemical Company concerning the particular application addressed in this test plan, three resins were selected for investigation. Two resins were recommended by Rohm and Haas (1990); Amberlite IRA-402° and IRA-410° (trademarks of Rohm and Haas Company, Philadelphia, Pennsylvania). Both these resins are conventional spherically shaped gel-type resins. Dow Chemical Company recommended Dowex 21K° (trademark of Dow Chemical Company, Midland, Michigan), also a gel-type resin.

The other principal physical form is the macroporous or macroreticular resins. The macroreticular resins have numerous pores throughout the resin particle effectively reducing the length of the solute diffusion path and thus increasing sorption/desorption rates compared to the conventional gel resins. Though not as physically rugged or kinetically fast as macroreticular resins, gel resins have higher exchange capacity and are less expensive.

All three resins selected for study are styrene-divinylbenzene copolymer matrices with quaternary ammonium functional (exchange) groups. The Amberlite IRA-402° and Dowex 21K° are Type I resins with benzyl-trimethylamine functionalities; the Amberlite IRA-410° is a Type II resin with benzyl-dimethylethan-olamine functionality. The Type II anion resin has slightly lower basicity than the Type I resin and requires less regenerant.

Before use, the test resins must be conditioned with an appropriate regenerant salt. In ion exchange, the ion(s) to be removed from solution will be exchanged for ions loaded on the resin. The exchange equilibrium is shown in the following reaction:

$$Rz^{+}X^{-} + C^{-} \neq Rz^{+}C^{-} + X^{-}$$
 (2)

where Rz⁺ is the resin polymer, X⁻ is the anion of the regenerant salt and C⁻ is the contaminant anion. The anion of the regenerant salt must be environmentally acceptable for discharge to the groundwater (preferably already present as a noncontaminant in the groundwater) and be chemically compatible

with the influent groundwater so that unwanted precipitation reactions do not occur in the column and cause hydraulic plugging. The salt itself must have high solubility to be an effective eluting agent for the contaminant-loaded column.

Sodium chloride (NaCl) and carbonate (Na $_2$ CO $_3$) are recommended (Dow 1988) for the regeneration of anion exchange columns used in uranium recovery operations. For application to the present studies, sodium chloride fulfills the criteria of being environmentally benign, present naturally in the Hanford groundwater and having high solubility for use as an eluant. The chloride ion will not react with species in the Hanford groundwater to cause an unwanted precipitation reaction in the column. Carbonate, however, may precipitate calcium carbonate (CaCO $_3$) in the column. Therefore, resin conditioning and regeneration by use of $4\underline{M}$ NaCl solution will be used in these tests.

Three sets of experiments are planned to evaluate the performance of the three resins for removal. The three sets of experiments are batch contact tests, breakthrough capacity column tests and load/elute cycling tests.

The effluent solutions will be analyzed spectrophotometrically for Cr(VI) concentration using the diphenylcarbazide reagent. The concentrations of total chromium will be determined by ICP spectrometry. The nitrate concentration will be determined by IC. The uranium concentration will be determined by laser fluorimetry. These determinations will be performed by Analytical Laboratory personnel.

After the best resin is selected, confirmatory tests (using the breakthrough column method) will be conducted on actual contaminated (both biodenitrification treated and untreated) Hanford groundwater.

4.6.2 Batch Contact Tests

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Batch resin/solution contact tests will be run for each test solution described in Table 4-1 with each of the three candidate resins. Two experiments, at 5 and 25 mL/g solution/wet conditioned resin ratio will be run for each test solution/resin combination. Contact times will be 30 min. Following contact, the mixtures will be centrifuged and the solutions analyzed for Cr(IV), total chromium, nitrate, and uranium.

Solute adsorption onto ion exchange resins generally follows the Freundlich adsorption isotherm:

$$y = kC^{n}$$
 (3)

where y is the quantity of solute adsorbed per mass of resin, C is the concentration of solute remaining in solution and k and n are constants. The quantity of the solute species on the resin is determined by difference between the quantities of solute found in the solution before and after resin contact. By taking logarithms of equation (3), the following equation is obtained:

$$\log(y) = \log(k) + n \log(C) \tag{4}$$

Therefore, plotting of log(y) on the y-axis versus log(C) on the x-axis will yield a straight line of slope n and a y-intercept of log(k). More importantly, by using this relationship, the resin loading at 100% breakthrough (where effluent concentration equals influent concentration) can be predicted and the capacity of the resin, in terms of throughput column volumes, calculated.

The experimental design allows four Freundlich plots to be made for each contaminant of interest. The four plots correspond to the four different concentration combinations of the remaining two contaminants. The solution number combinations for the four Freundlich plots for each contaminant are shown in Table 4-2. Because two different solution-to-resin ratios are used (5 $\,$ mL/g and 25 $\,$ mL/g), four well-spaced points will be obtained for each log-log Freundlich plot.

The projected contaminant breakthrough capacities found for each resin and co-contaminant level will be calculated and compared. Based on the results of the batch tests, one (or perhaps two) resin(s) will be selected for breakthrough capacity column tests and load/elute tests.

Table 4-2. Solution Numbers to be Used in Freundlich Plots.

	Contamina	Solution			
Contaminant	Cr(VI)	U(VI)	NO ₃	Numbers*	
Chromate		800	200,000	1 + 5	
		800	2,000	2 + 6	
		40	200,000	3 + 7	
		40	2,000	4 + 8	
Uranium	2,000		200,000	1 + 3	
	2,000		2,000	2 + 4	
	50		200,000	5 + 7	
	50		2,000	6 + 8	
Nitrate	2,000	800		1 + 2	
	2,000	40		3 + 4	
	50	800		5 + 6	
	50	40		7 + 8	

^{*} Solution number and concentrations from Table 4-1. Note that two different solutions are referenced, and therefore, the concentration of the contaminant whose value is different for the two solutions is not listed here.

4.6.3 Breakthrough Capacity Column Tests

Using the test solution number 1 from Table 4-1, breakthrough capacity tests will be conducted for the resin(s) of interest. Solution 1 is chosen because it presents the highest loading for the columns. Columns having approximate 1-cm diameter and 5-cm length of resin will be prepared in the chloride form. The quantity of wet resin introduced to the column will be determined by weighing and the diameter and length of the resin bed measured.

Using a metering pump, test solution number 1 will be introduced to the resin column upflow (i.e., from the bottom up) at the rate of about 60 mL/h. This loading rate corresponds to about 16 bed volumes (column volumes) per hour at the resin column dimensions described and is typical in ion exchange application. Effluent samples will be collected periodically, as described below, and the solutions analyzed for chromate, total chromium, uranium and nitrate. The breakthrough of the contaminants will be monitored via the analytical results.

The breakthrough tests will be run until the volume passed through the column is 120% of the breakthrough capacity of the contaminant having the highest predicted breakthrough capacity. From 15 to 20 column effluent samples will be collected for analysis at points approximately evenly spaced in the breakthrough test column loading.

The volume of solution corresponding to 120% breakthrough for each of the three contaminants is predicted via the Freundlich isotherm results from the batch contact tests described in Section 4.3.2. The breakthrough capacity for each contaminant at the test solution 1 composition is predicted by the Freundlich isotherm plots of the following batch test results:

<u>Contaminant</u>	<u>Solution Numbers</u>
Chromate	1 + 5
Uranium	1 + 3
Nitrate	1 + 2

At equal contaminant concentrations, the affinity of the four contaminant species for the resin is expected to increase in the order:

$$NO_3^- < CrO_4^{2-} < UO_2(CO_3)_2^{2-} < UO_2(CO_3)_3^{4-}$$

However, in test solution 1, the concentration of nitrate dominates the concentrations of the chromate and uranium species and thus will compete strongly for exchange sites on the resin despite its lower affinity for ion exchange sites. Solution 1 therefore, is the solution presenting the most difficult test for the ion exchange system. Sulfate ion present naturally in the water also may compete.

Breakthrough tests will also be performed with contaminated groundwater (treated by a biodenitrification process under development at Pacific Northwest Laboratory (PNL)).

4.6.4 Load/Elute Cycling Tests

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To test the resilience of the selected resin for in-process use, repeated (at least 10 cycles of) loading and eluting of the resin will be performed. Solution number 1, described in Table 4-1, will be the solution used in the cycling tests. Solution 1 is chosen because it presents the highest loading for the columns. A 1-cm diameter by 5-cm long column similar to the column described in Section 4.3.3 will be prepared and the solution loaded upflow.

The column will be loaded at about 16 column volumes per hour until the volume necessary for the first contaminant to reach 50% breakthrough is achieved. The volume at 50% breakthrough will be derived from the data gathered in breakthrough tests described in Section 4.3.3. The column will then be eluted, downflow, using $4\underline{M}$ NaCl solution. The efficiency of the eluant will be tested during the first elution by collecting eluate samples and analyzing the samples for chromate, total chromium, uranium and nitrate. The projected eluant volume is 1.5 to 2.5 column volumes (Rohm 1990).

Following elution, the column will be washed, downflow, with water and prepared for the next load cycle. About 10 column volumes should be sufficient (Rohm 1990). Qualitative checking for the presence of chloride ion in the wash may be performed using silver nitrate $(AgNO_3)$ solution.

For each load cycle, effluent solution samples will be gathered at about 4 or 5 points in the cycle. The samples will be analyzed for chromate, total chromium, uranium and nitrate. The load, elute and wash cycle will be repeated at least nine more times and the efficiency of the column for removal of the three contaminants evaluated. At the last cycle, elution samples will again be gathered and analyzed to retest the efficiency of the NaCl eluant.

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APPENDIX A SCHEDULE OF ACTIVITIES

Westinghouse Hanford Company

Internal Memo

From: Laboratory Scheduling and Work Control
Phone: 3-3883 T7-25
Date: January 28, 1993
Subject: Groundwater Treatability Tests

12630-93-06

To:

M. L. Bell

T6-16

T6-16

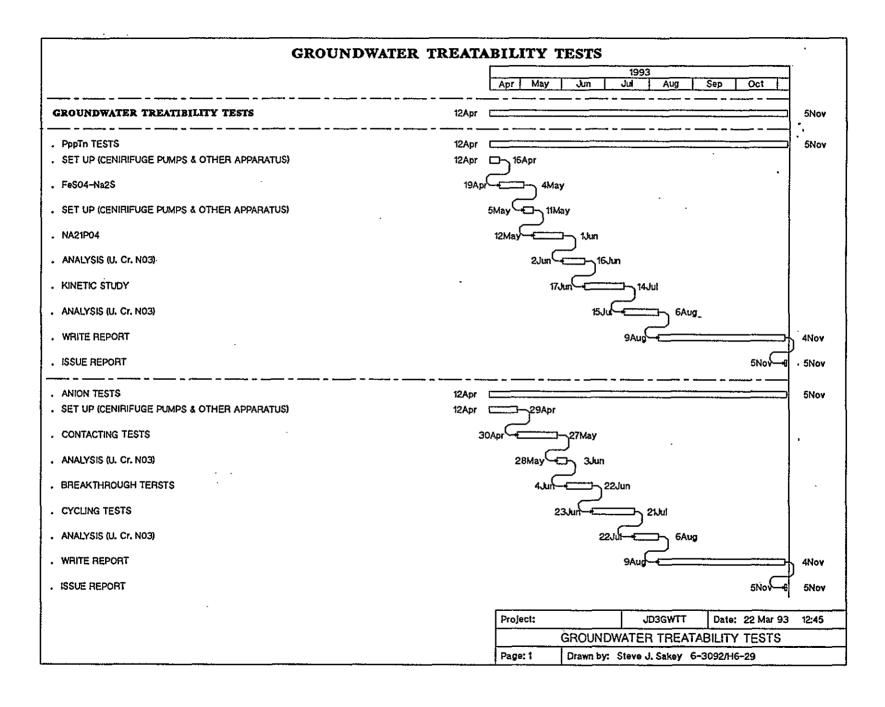
cc: E. J Kosiancic JLZ; JGP; WMS File/LB

Attached is the Groundwater Treatability Tests Laboratory Schedule for your review and approval. All dates are subject to test procedure document approval WHC-SD-EN-TC-003 and will be adjusted accordingly.

If there are any questions, please call Bill Smithers on 373-3883, or mail to T7-25.

Kristofzski

Hanford Operations and Engineering Commeter for the US Department of Energy



A-3

APPENDIX B TREATMENT OF URANIUM-BEARING GROUND WATERS WITH PHOSPHATE

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Internal Letter



Rockwell International

October 21, 1985

No . 65454-85-143

TO:

V. W. Hall

Waste Management Program Office

2750E/200 È

FROM: (Name, Organization, Internal Address, Phone)
C. H. Delegard
Pu Process Development Unit

234-5/200 W

3-3723

Subject: Treatment of Uranium-Bearing Ground Waters with Phosphate

Discovery of high uranium concentrations (up to 0.1 g U/L or ~60,000 pCi/L) in the unconfined aquifer underlying the 216-U-1/-2 cribs in the Hanford 200 West Area in early 1985 has led to remedial action to remove the uranium from the groundwater. The remedial action that has been taken is to pump the uranium-bearing groundwater from a well near the center of the plume and pass the water through a bed of anion exchange resin. The uranium, present as the triscarbonato uranyl anion, is sorbed on the resin while the decontaminated groundwater is disposed to the ground. The uranium is eluted from the resin bed by 2 M ammonium nitrate and is disposed to underground high-level waste storage tanks.

Since the object of the above remedial action is to decontaminate the groundwater without concurrent uranium recovery, other possibly less-costly methods may be considered. One method which may merit consideration is carrier precipitation of the uranium using the mineral brushite, CaHPO.

Some experiments conducted early in the U-1/-2 investigations centered on various precipitation techniques to remove uranium from the groundwater. Of the several methods tested, which included pH adjustment using NaOH and KOH and addition of chemical reductants, addition of NaH_2PO_4 to the groundwater was found to give the greatest decontamination. Sufficient 1 M NaH2PO4 was added to the groundwater to make the resulting solution 0.01 M in NaHoPO4. Reaction of the NaHoPO4 with the calcium ion present at ~0.01 M in the groundwater resulted in the precipitation of the mineral brushite, CaHPO4. In precipitating, the brushite carried down uranium and reduced the uranium solution concentration 1000-fold to ~10-4 g/L (~60 pCi/L), well below Table II limits.

If the uranium concentration can be reduced to less than Table II limits for solution pumped from the U-1/-2 plume by coprecipitation with brushite, simple ground disposal of the phosphate-treated suspension may be feasible. The uranium trapped in the brushite would be filtered by the Hanford sediments and would be retained in a solid phase well above the water table. The decontaminated solution could drain to the water table. The disposition of uranium in the sediment would be comparable to the disposition of radioactive strontium or cesium as currently practiced in Hanford low-level waste disposal to the ground.



V. W. Hall Page 2

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To demonstrate the feasibility of this approach, laboratory and field experiments need to be conducted. The aims of the experiments would be:

- Demonstrate in the laboratory that brushite precipitation will decontaminate less-concentrated U-1/-2 solutions to below Table II limits.
- 2. Determine the filterability of the brushite by Hanford sediments in lab and field experiments.
- 3. Determine in lab and field tests the hydraulic permeability of the sediments as a function of brushite loading to determine the size of crib necessary to dispose the treated groundwater.

Before undertaking lab and field tests, however, an engineering feasibility study must be conducted to answer the following questions:

- Is return of the uranium to the ground, albeit in a non-mobile form, acceptable by current DOE and Washington State regulations; is it acceptable politically.
- 2. If ground disposal is not acceptable, can filtration or other solids removal techniques be applied; what happens to the uranium-bearing solids.
- 3. How do the costs of phosphate treatment in its various options compare to the currently practiced ion exchange technique.

Please call if you have questions or would like to discuss this proposal further.

C. H. Delegard Senior Chemist

CHD:gij

cc: T. A. Lane

R. C. Routson

J. P. Sloughter

APPENDIX C

URANIUM SOLUBILITY AND SORPTION ONTO HANFORD SEDIMENT IN NEUTRALIZED UO3 PLANT PROCESS CONDENSATE

Internal Letter



Rockwell International

Dale.

June 8, 1987

TO:

(Name Organization, Internal Address)

- . D. M. Tulberg
- . Environmental Engineering
- . 2750E/D204/200E

FROM: Name, O-gan-zation, Internal Address, Phone)

- . C. H. Delegard
- . Pu Process Development
- 234-5Z/200W

. 65454-87-081

3-3723

Subject. . Uranium Solubility and Sorption onto Hanford Sediment in Neutralized ${\rm UO_2}$ Plant Process Condensate

Refs: See attached.

Introduction

Process condensates (UPC) discharged from the UO₃ Plant have been shown by U.S. Testing to be essentially a nitric acid (HNO₃) solution containing trace levels of stainless steel corrosion products (Fe, Cr, Ni). . Also present is uranium (U), whose concentration has recently averaged 4000 pCi per liter (approximately 6 mg U per liter). The current practice of disposal of this acidic stream to the sediments of the 216-U-17 crib requires neutralization to meet environmental discharge guidelines regarding pH. In the absence of a pH buffer, pH control of this strong acid neutralization under plant conditions is difficult.

Phosphate has been proposed as a potential buffering agent since neutralization of the ion $\rm H_2PO_4^-$ to yield $\rm HPO_4^{2-}$ occurs at about pH 7 (Weiss, 1986). Phosphate also may limit U concentrations in the neutralized and discharged UPC by its reaction with calcium ion in the sediment to form the mineral brushite (CaHPO_4). Brushite precipitation has been shown (Muller, 1984 and Delegard, 1985) to coprecipitate or carry down U from dilute solutions. Final U concentrations as low as 0.1 mg per liter even in the presence of 0.01M bicarbonate have been attained (Delegard, 1985). The presence of high concentrations of phosphate in Bismuth Phosphate process discharges also was postulated to limit the migration of four tonnes of U in the 216-U-1 and -2 cribs. This postulation was based on the discovery of the mineral calcium autunite, a calcium uranyl phosphate, high in the 216-U-1,2 crib sediment column (Delegard, et al., 1986). The effect of phosphate on the sorption of U onto Hanford sediments, however, has not been studied in detail.

Accordingly, a request was made (Tulberg, 1987) to study the solubility and sorption of uranium onto Hanford sediment in a simulated KOH-neutral-ized UPC as a function of pH and phosphate addition. Separate solubility and sorption experiments were performed in our laboratory to evaluate these effects. The tests performed and the test results are described and evaluated in this report.

Summary and Conclusions

The effects of phosphate addition (0.004 \underline{M} phosphoric acid) and pH (at about pH 5, 7, 8.5, 9, 10 and 11) on the solubility of uranium in KOH-neutralized simulated UPC solution, and on the sorption of the dissolved



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uranium onto the Hanford sediment, was studied. The simulated UPC was $0.1\underline{\text{M}}$ HNO3 and 6.0 mg U (as U(YI) nitrate) per liter. As expected, KOH titration experiments showed addition of phosphate helped buffer the solution pH at about pH 7.

In the solubility tests, U-bearing solids precipitated under all conditions except for a pH 5 test having no added phosphate. The uranium phase found in pH 7, 8.5, 9, 10 and 11 tests having no phosphate was identified by X-ray diffractometry to be the mineral schoepite, $UO_2(OH)_2 \cdot 2H_2O$. Uranium solution concentrations in the presence of schoepite ranged from 10^{-0} to $10^{-7}M$ (about 160 to 16 pCi U per liter). With phosphate present, the pH 5, 7, 8.5, 9 and 10 tests yielded precipitates identified as autunite $(H_2(UO_2)_2(PO_4)_2)$ and/or potassium autunite $(K_2(UO_2)_2(PO_4)_2)$. Uranium solution concentrations ranged from 10^{-7} to $2xIO^{-9}M$ (about 16 to 0.4 pCi U per liter). At pH 11 with phosphate present, schoepite and another, unidentified, phase were detected. Uranium solution concentration in this test was about $3xIO^{-0}M$ (500 pCi U per liter).

The U-bearing supernatant solutions from the solubility tests were contacted with Hanford sediment and the sorption of U onto the sediment determined after one week's equilibration. Final U solution concentrations and distribution coefficients (Kd's) were evaluated for these tests. For the tests without phosphate addition, final U concentrations ranged from 10^{-5} to $3\times10^{-9} \text{M}$ (1600 to 0.5 pCi U per liter) and Kd's ranged from about 10 to 400 mL per gram. The pH of the suspensions before contact had been adjusted to range between 5 and 11. Buffering reactions with the sediment reduced the final pH range to 7.7 to 8.7. For the tests with phosphate addition, final U concentrations ranged from 6×10^{-9} to $8\times10^{-10} \text{M}$ (about 1 to 0.1 pCi U per liter) and Kd's ranged from 5 to 5000 mL per gram. Buffering reactions with the sediment reduced the pH range from 5-11 to 6.8-8.9.

Based on these results, phosphate addition to the UPC is recommended. The addition of phosphate supplies a buffering agent to aid pH adjustment of the UPC. The phosphate also reduces solubility-controlled U concentration in the KOH-neutralized UPC in the pH range of 5 to 10 as compared to the UPC without phosphate. Sorption and/or precipitation reactions with the sediment further serve to reduce U solution concentrations. The U solution concentrations are lower over a broader pH range in the presence of phosphate than without phosphate.

Experimental Materials and Methods

Simulated UPC was prepared using reagent-grade HNO $_3$ and 530 g U per liter uranyl nitrate stock. Reagent-grade phosphoric acid (H $_3$ PO $_4$) was added as required. Two stock solutions were prepared. Both had 0.10M HNO $_3$ and 6.0 mg U per liter. The phosphate-bearing stock solution also contained



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 $0.0040 \underline{M} \text{ H}_3 \text{PO}_4$. A pH titration of each stock solution was run using $10 \underline{M}$ KOH.

One-hundred mL aliquots of the stock solutions were measured and the pH values adjusted to approximately 5, 7, 8.5, 9, 10 and 11 using $10\underline{M}$ KOH solution. The pH-adjusted solutions were set aside for 3-4 days and then filtered through 0.003 μ m pore size Amicon type CF50A polysulfone ultrafilters. The pH's of the solutions were measured and a sample of each filtrate set aside for U concentration analysis.

Yellow-colored solids were collected in the filters for all solutions except the pH 5 test having no added phosphate. The solids were prepared and examined by X-ray diffractometry.

A sample of sediment from the 20-foot depth of well 299-W19-90 was provided by the Environmental Engineering Unit. This well lies near the affected 216-U-17 crib and is taken from the same depth as the UPC discharge pipe. The sediment sample was apportioned to approximately 5-gram subsamples using the cone and quarter technique. The subsamples were weighed into 50-mL polycarbonate Oak Ridge style centrifuge tubes. Thirty milliliters of pH-adjusted UPC then were added to each sediment portion. Triplicate experiments were prepared for each pH/phosphate condition. The solution and sediment samples were shaken briefly and the solution pH readjusted with HNO3 or KOH solution to approximately the original solution pH. The solution/sediment suspensions were capped tightly, set on a reciprocal shaker and agitated at about 1 Hz, 6-inch amplitude, at room temperature.

After one week's contact, the agitation was stopped and the supernatant solutions ultrafiltered and sampled for uranium concentration. The pH values of the suspensions were determined and recorded.

Uranium concentrations were determined by laser fluorimetry by personnel in the Research Support Group. X-ray diffraction analyses were performed by R. L. Wilson of the Analytical Chemistry Group. Both groups are part of the Analytical Laboratory Department of Safety and Quality Assurance.

Results and Discussion

Titration results of the simulated UPC solutions with KOH solution are presented in figure 1. As expected, the UPC solution without added phosphate showed typical strong acid-strong base titration behavior in that transition through neutral pH (\sim 5 to 9) occurred with only minimal change in added titrant. The UPC having added phosphate, on the other hand, showed a pH inflection of about pH 7. This inflection corresponds to the buffering reaction of ${\rm H_2PO_4^2}$ to ${\rm HPO_4^2}$. The relative titrant volume width of this buffering region is proportional to the ratio of the concentration of added phosphate to the total concentration of acid in the UPC. Thus, the buffering region of the phosphate-bearing UPC is



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about 0.004 (\underline{M} H₃PO₄)/[0.01 (\underline{M} HNO₃) + 2x0.004 (\underline{M} H₃PO₄)] or 4 percent of the total titrant volume.

The analytical data and Kd values for the various solubility and sorption experiments are presented in the table. The uranium concentration data in the KOH-neutralized synthetic UPC solutions are presented in figure 2. The total added uranium concentration in these solutions was 6 mg per liter or about $10^{-4} \cdot {}^{7} \underline{\text{M}}$. However, precipitation of U-bearing solids occurred in all test solutions except the pH 5 test having no added phosphate. The solubility-limited U concentrations in the tests without phosphate were 10^{-6} to $10^{-7}\underline{\text{M}}$ or about 160 to 16 pCi U per liter. With phosphate present, U concentrations were solubility-limited to the range $3\times10^{-6}\underline{\text{M}}$ (at pH 11) to a minimum of $2\times10^{-9}\underline{\text{M}}$ (at pH 7) or about 500 to 0.4 pCi U per liter.

X-ray diffraction analyses of the solids showed schoepite $(UO_2(OH)_2 \cdot 2H_2O)$ to be present in the pH 7, 8.5 and 11 tests having no added phosphate. The flat solubility curve of schoepite between about pH 8 and 11 suggests $UO_2(OH)_2^O$ is the dissolved species in this range. Cationic species such as UO_2OH^+ prevail at lower pH. No evidence of anionic species, as would be shown by increased solubility at higher pH, was found. These data are in general agreement with solubility and speciation data for U as reviewed by Krupka, et al. (1983) and Allard (1982). The solubility—limited U concentrations, however, are as much as 1000 times lower than concentrations found in similar experiments reported by Krupka, et al. (1985).

Since the present experiments were conducted starting with acidic U solutions and $10\underline{M}$ KOH, little carbonate was expected to be present in the test solutions. In the presence of sufficient carbonate, however, schoepite is not expected to form due to carbonate complexation of the uranium.

Diffraction analyses of the solids formed in the tests with phosphate present showed autunite $(H_2(UO_2)_2(PO_4)_2)$ and/or potassium autunite $(K_2(UO_2)_2(PO_4)_2)$ in the pH 5, 7, 8.5, 9 and 10 tests while schoepite and another, unidentified, phase formed in the pH 11 test. Potassium uranate phases gave similar, but not matching, X-ray diffraction patterns compared to the unassigned diffraction peaks from the pH 11 test. Solubility data for autunites are scarce in the technical literature. The reviews by Krupka, et al. (1983) and Langmuir (1978) show little information available on autunite solubility at near-neutral pH (most data are for pH \sim 1-4). The present data indicate that the autunite(s) controlled dissolved U concentrations at or below the schoepite solubility at pH's from at least 5 to 10. Above pH 7, complexing of the U by HPO₄²⁻¹ to form species such as UO₂(HPO₄)₂²⁻¹ presumably was responsible for increasing U concentrations. At pH 11, when the autunite solid phase gave way to schoepite, further complexing resulted in dissolved U concentrations higher than those found in the tests without phosphate.



International

D. M. Tulberg Page 5 June 8, 1987

Sorption tests of the filtered U-bearing UPC solutions with Hanford sediment were conducted. The test data are presented in the table. Distribution coefficient (Kd) values were calculated and are also given in the table. The pH values of the sediment/solution mixtures were adjusted to approximately the original solution pH. However, after the one week contact, the pH's of the mixtures were buffered to intermediate values presumably by sediment-solution reactions. The pH changes which occurred (presented in the table) ranged from an increase of about 3 pH units (from pH ~5 to 8) to a decrease of about 2 pH units (from pH ~11 to 9) for the tests without phosphate. The phosphate helped control the mixtures' pH's closer to the original pH values. Thus, the pH increased only about 2 pH units (from pH ~5 to 7) at the low pH end and decreased about 2 pH units at the high pH end for the tests with phosphate.

While the U Kd's were evaluated in these tests, perhaps more meaningful are the final U concentrations from the sorption experiments. The final uranium concentration data are shown in figure 3. The Kd values for the tests without phosphate are lowest where the initial uranium concentrations are highest. At higher pH, where initial uranium concentrations are low, Kd's are high. The net effect, as shown in figure 3, is that final U concentrations in solution for tests without phosphate are extremely pH dependent. In contrast, the final uranium solution concentrations for the tests with phosphate are uniform and lower over the wide pH range studied. The reason for the low U concentrations for the phosphate tests is not clear. However, the coprecipitation of uranium with CaHPO₄ (brushite) formed from reaction of phosphate with calcium ion present in the sediment seems to be the most likely explanation of the mechanism of uranium removal from the solution.

C. H. Delegard Staff Chemist

CHD/p.im

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cc: L. L. Adams

M. R. Adams

G. S. Barney

D. L. Flyckt

V. W. Hall

D. C. Hedengren

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K. L. Mudge

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M. R. Schwab

G. C. Shirey

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Letterbook

Process Aids



D. M. Tulberg Page 6 June 8, 1987

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Figure 1 Titration of 0.1M HNO $_3$ With and Without 0.004M H $_3\text{PO}_4$ Using 10M KOH

KOH Titration of UO3 Plant Condensates

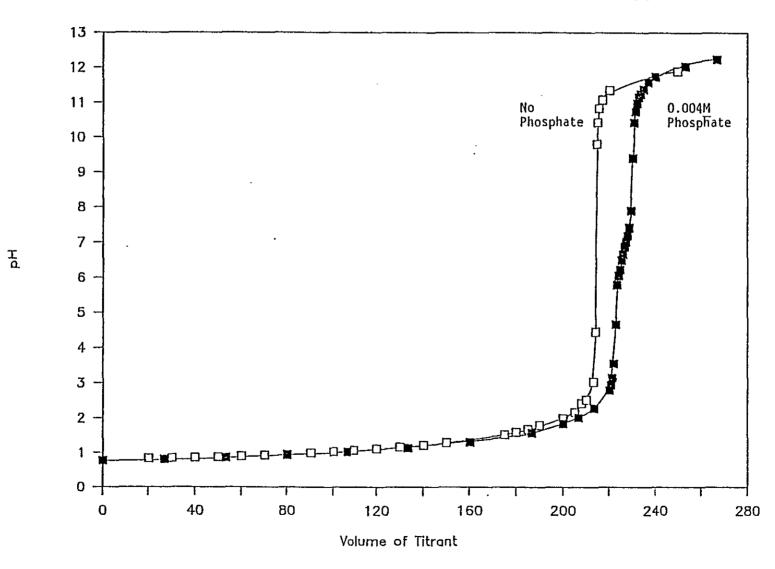
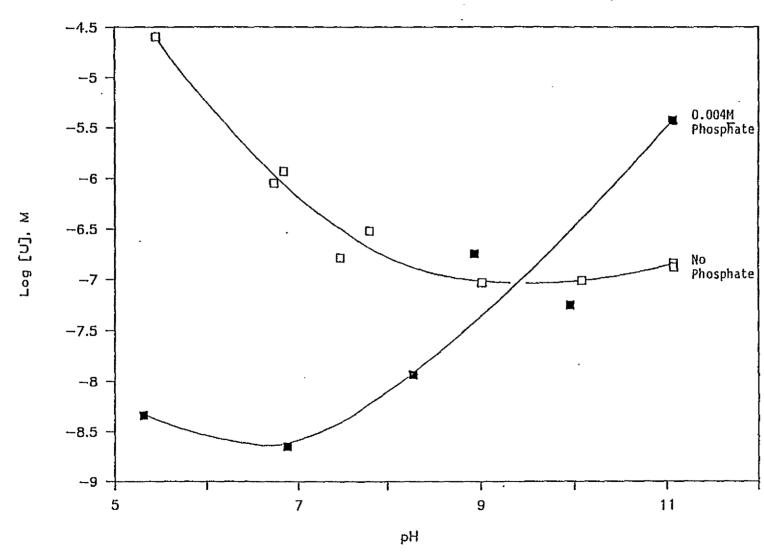


Fig...e 2 Dissolved Uranium Concentration in KOH-Neutralized 0.1M HN03 With and Without 0.004M $\rm H_3P0_4$ as a Function of pH

Uranium Concentration Versus pH



[U] in Solutions with Sediment

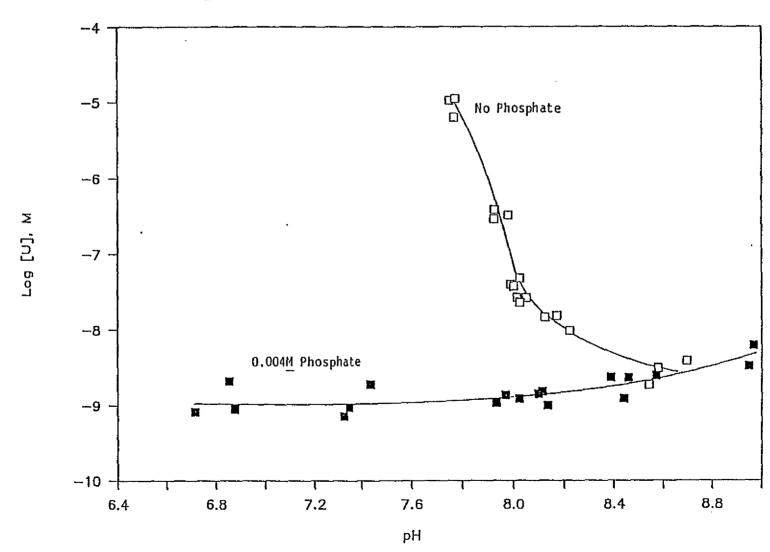


Table: Exp mental Data

				lante.	••	icui Daca	•				
Sample*	Soin. pH	Sed. Wt. (grams)	In. [U] (g/L)	Log (V)i	Fin. LU] (g/L)	Log (U)f (M)	In. pH	Fin. pH p	H Change	15d (nL/g)	
IJN5-1	5.149		6.00E-03		1.51E-03	-5. 178	5.025	7.768	2.743	18.1	
UN5-2	5.449		6.008-03		2.64E-03		5.219	- 7.773	2.554	7.6	
UN5-3	5.449		6.00E-03		2.51E-03	-4.977	4.908	7.749	2.841	9.1	
IJN7−1	6.726	4,789	2,13E-04	-6.048	6.84E-05	-6.542	6.434	7.924	1.49	13.2	
UN7-2	6.726	4.471	2.13E-04	-6.049	7.726-05	-6.489	6.963	7.98	1.017	11.8	
NN1-3	6.726	4.529	2.13E-04	-6.048	9.13E-05	-6.416	7.137	7.924	0.787	9.8	
ยพย-1	7.453	4.483	3,93E-05	-6. 702	1.13E-05	-7.323	8.484	8.024	-0.458	16.6	
UN8-2	7.453	4.854	3.93E-05	-6.782	9.41E-06	-7.403	9.479	7.989	-0.51	19.6	
UNG-3	7.453	4.063	3.93E-05	-6.702	8.846-04	-7.429	8.536	8.002	-0.534	21.2	
UN9-1	9.011	5.751	2.20E-05	~7.034	6.246-06	-7.581	8.984	8,052	-0.932	13.2	
UN9-2	9.011	5.076	2.20E-05	-7.034	6.276-04	~7.579	7,002	8.015	-0.987	14.0	
UN9-3	7.011	4.819	2.20E-05	-7.034	5.40E-06	-7.644	8.854	8.026	-0.828	19.1	
UN10-1	10.08	4.736	2.326-05	-7.011	3.486-04	-7.835	9.742	B.127	-1.615	35.9	
UN10-2	10.08	4,454	2.32E-05	-7.011	2.30E-06	-8.015	9.974	8.223	-1.751	61.2	
UN10-3	10.08	5.934	2.32E-05	-7,011	3.65E-04	-7.814	9.874	8.172	-1.702	27.1	
UN11-1	11.075	5.363	3.106-05	-6.074	9.12E-07	-8.417	10.771	8.679	-2,072	169.5	
UN11-2	11.075	5.382	3.18E-03	-6.874	7.38E-07	-8.509	10.948	8.579	-2.369	234.6	
NN11-3	11.075	5.125	3.106-05	-6.874	4.43E-07	-0.730	11.031	8.542	-2,489	414.3	
UPS-1	5,312	4.881	1.09E-06	-0.339	4.99E-07	-8.678	5.079	6.854	1.775	7.3	
UP5~2	5.312	4.083	1.09E-06	-0.339	2.12E-07	-9.050	4.805	6.B78	2.073	25.5	
UP5-3	5,312	4.046	1.09E-06	-8.337	1.97E-07	-9.082	4.714	6.714	2	33.6	
UP7~1	4.872	5.519	5.30E-07	-0.652	1.71E-07	-9.144	6.791	7.319	0.528	11.4	
UP7-2	4.872		5.30E-07		4.53E-07	-8.720	7.018	7.439	0.421	1.0	
ロドケース	6.872	5.799	5.30E-07	-U.652	2.24E-07	-9.026	6.919	7,343	0.424	7.1	
UPB-1	0.274		2.786-06		2.56E-07	-0.960	8.266	7.932	-0.334	54.3	
UF:8-2	8.274		2.786-06		2.896-07	-8.916	8.572	8.024	-0.548	49.3	
UF8-3	8.274	4.940	2.706-06	-7.933	3.24E-07	-8.866	8.493	7.969	-0.524	45.8	
UP9-1	8.931		4.30E-05		3.59E-07	-8.821	B.941	8.116	-0.825	796.6	
UP9-2	B. 931		4.306-05		3.36E-07	-8.850	9.055	8.1	-0.955	630.4	
ロアターズ	8.931	5.659	4.30E-05	-4.743	2.36E-07	-9.004	9.99	8.137	-0.853	960.6	
UP10-1	9.953		1.34E-05		5.55E-07	-8.632	9.945	8.387	-1.558	117.9	
UP10-2	9.953		1.34E-05		2.95E-07	-0.907	10.024	8.439	-1.585	235.7	
UP10-3	9.953	6.259	1.34E-05	7.219	5.54E-07	-8.633	10.026	8.45B	-1.568	111.1	
UP11-1	11.066		8.92E-04		7.816-07	-0.404	11-043	8.948	-2.095	6987.9	
UP11-2	11.066		8.92E-04		1.40E-06	-8.206	10.986	B. 967	-2.019	3033.3	
UF-11-3	11.046	5.485	B.92E-04	-5.426	5.84E-07	-0.610	11.085	B.57	-2.515	8348.6	
UN7-R	6.832		2.700-04								
UNB-R	7,806		7.198-05								
UNII-R	11.073		3.466-03	-6.039	5						

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^{*}Sample number code: It = no phosphate; P = phosphate; 5,7,8,9,10,11 = approx. pH; 1,2,3 = replicate number

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